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Honeywell Docket No. 300-9 (4010)

HIGHLY STABLE PACKAGING SUBSTRATES

Field of The Invention

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The field of the invention is electronic packaging materials.

Background of The Invention

5 Almost all electronic circuits require some form of packaging, which typically involves polymeric materials. In general, polymeric materials utilized in packaging applications must have a broad range of desirable physical properties. These properties include low coefficient of thermal expansion (CTE), thermal stability, high glass transition temperature, low moisture absorption, and adhesion to metal (Cu, Cr) and polymers. Further desirable properties include
10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 1245 1250 1255 1260 1265 1270 1275 1280 1285 1290 1295 1300 1305 1310 1315 1320 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440 1445 1450 1455 1460 1465 1470 1475 1480 1485 1490 1495 1500 1505 1510 1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 1565 1570 1575 1580 1585 1590 1595 1600 1605 1610 1615 1620 1625 1630 1635 1640 1645 1650 1655 1660 1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 1715 1720 1725 1730 1735 1740 1745 1750 1755 1760 1765 1770 1775 1780 1785 1790 1795 1800 1805 1810 1815 1820 1825 1830 1835 1840 1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 1895 1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015 2020 2025 2030 2035 2040 2045 2050 2055 2060 2065 2070 2075 2080 2085 2090 2095 2100 2105 2110 2115 2120 2125 2130 2135 2140 2145 2150 2155 2160 2165 2170 2175 2180 2185 2190 2195 2200 2205 2210 2215 2220 2225 2230 2235 2240 2245 2250 2255 2260 2265 2270 2275 2280 2285 2290 2295 2300 2305 2310 2315 2320 2325 2330 2335 2340 2345 2350 2355 2360 2365 2370 2375 2380 2385 2390 2395 2400 2405 2410 2415 2420 2425 2430 2435 2440 2445 2450 2455 2460 2465 2470 2475 2480 2485 2490 2495 2500 2505 2510 2515 2520 2525 2530 2535 2540 2545 2550 2555 2560 2565 2570 2575 2580 2585 2590 2595 2600 2605 2610 2615 2620 2625 2630 2635 2640 2645 2650 2655 2660 2665 2670 2675 2680 2685 2690 2695 2700 2705 2710 2715 2720 2725 2730 2735 2740 2745 2750 2755 2760 2765 2770 2775 2780 2785 2790 2795 2800 2805 2810 2815 2820 2825 2830 2835 2840 2845 2850 2855 2860 2865 2870 2875 2880 2885 2890 2895 2900 2905 2910 2915 2920 2925 2930 2935 2940 2945 2950 2955 2960 2965 2970 2975 2980 2985 2990 2995 3000 3005 3010 3015 3020 3025 3030 3035 3040 3045 3050 3055 3060 3065 3070 3075 3080 3085 3090 3095 3100 3105 3110 3115 3120 3125 3130 3135 3140 3145 3150 3155 3160 3165 3170 3175 3180 3185 3190 3195 3200 3205 3210 3215 3220 3225 3230 3235 3240 3245 3250 3255 3260 3265 3270 3275 3280 3285 3290 3295 3300 3305 3310 3315 3320 3325 3330 3335 3340 3345 3350 3355 3360 3365 3370 3375 3380 3385 3390 3395 3400 3405 3410 3415 3420 3425 3430 3435 3440 3445 3450 3455 3460 3465 3470 3475 3480 3485 3490 3495 3500 3505 3510 3515 3520 3525 3530 3535 3540 3545 3550 3555 3560 3565 3570 3575 3580 3585 3590 3595 3600 3605 3610 3615 3620 3625 3630 3635 3640 3645 3650 3655 3660 3665 3670 3675 3680 3685 3690 3695 3700 3705 3710 3715 3720 3725 3730 3735 3740 3745 3750 3755 3760 3765 3770 3775 3780 3785 3790 3795 3800 3805 3810 3815 3820 3825 3830 3835 3840 3845 3850 3855 3860 3865 3870 3875 3880 3885 3890 3895 3900 3905 3910 3915 3920 3925 3930 3935 3940 3945 3950 3955 3960 3965 3970 3975 3980 3985 3990 3995 4000 4005 4010

Many polymeric materials for packaging electronic circuits are known in the art, and can be categorized into various classes according to their chemical composition. For example, one class of polymeric materials comprises polyimides that are commonly found in fibers, coatings, and films. However, polyimides exhibit several drawbacks, including high moisture absorption, dimensional movement associated with moisture absorption, poor adhesion to some substrates, shrinkage at high temperatures, and a sidedness to films such that each side of the film may have very different properties.

In another class the polymeric materials comprise epoxy compounds. Polymeric materials made from epoxy compounds typically have a glass transition temperature of about 140°-220°C and generally exhibit a moisture absorption of about 1-4%. While relatively inexpensive, most epoxy- based packaging compounds generally require drying and/or heat stabilization steps to allow their use in high density interconnect applications. For example, styrene-maleic anhydride/epoxies often exhibit desirable electrical and moisture properties. However, such epoxies having glass transition temperatures above 230° C are generally difficult to manufacture, and frequently exhibit an undesirably high coefficient of thermal expansion.

In a further class the polymeric materials comprise polyarylenes. Polyarylenes are thermally stable polymers, but are often difficult to process due to relatively low solubility in

common organic solvents. A number of different routes for the preparation of high molecular weight polyarylenes soluble in organic solvents have been proposed. In one route, as shown for example in U.S. Pat No. 5,227,457, Marrocco, III, M., et al. describe the introduction of solubilizing groups such as phenyls onto the polymeric chain. Unfortunately, the solubilizing 5 groups may also render the resultant polymer sensitive to processing solvents. In another route, for example U.S. Pat. No. 5,334,668 to Tour, J., et al. crosslinkable polyphenylene compositions are prepared having a relatively low molecular weight initially, but form upon heating crosslinked polymers exhibiting increased solvent resistance. However, these compositions may have among other disadvantages insufficient gap filling properties.

10 In view of the problems of various prior art polymeric compounds for electronic packaging, phenylethynyl substituted aromatic polymeric materials have been developed. Phenylethynyl and acetylene substituted compounds are well known [*High Performance Thermosets*, ed. Shiow-Ching Lin & Eli M. Pearce, Hanser Publishers, New York, 1993, pg 221], and generally confer the advantage that they can be thermally induced to crosslink to form 15 fused aromatic compounds. More advantageously, crosslinking of phenylethynyl and acetylene substituted aromatic polymeric materials can be performed in the complete absence of polar functionalities when carbon atoms in an aromatic compound are substituted with phenylethynyl groups. For example, in U.S. Pat. No. 4,730,032, Rossi et al. teach phenylethynyl functionalized aromatic compounds which crosslink in a temperature range of about 270-330°C. In another 20 example, phenylethynyl substituted polymers with relatively high glass transition temperatures have been developed [*Polym. Prep.*, Am. Chem. Div., Polym. Div., 28(1), 67 (1987)], and in a further example, WO 97/10193 to Dow Chemical Company, bis(o-diethynyl) monomers as shown in prior art **Figure 1** are described.

However, some problems still persist with phenylethynyl or acetylene substituted 25 aromatic polymeric materials. First, a relatively high level of a palladium based catalyst is required which may lead to subsequent problems in purification. Second, in order to produce phenylethynyl substituted aromatic compounds such as bis(ortho-diphenylyethynyl) aromatic compounds, a multistep synthesis is typically required, disadvantageously increasing the cost of the synthesis. Third, because most of the phenylethynyl substituted aromatic compounds are 30 designed for direct use on/with semiconductors (integrated circuit encapsulants), high thermal

stability is required. However, high thermal stability often demands for non-halogenated products frequently resulting in arduous processes to insure the absence of halogens. Still further, crosslinked phenylethynyl substituted aromatic compounds tend to be brittle, and often require relatively high temperatures for complete curing.

5 In spite of various polymers having been developed for packaging of electronic circuits, almost all such polymers suffer from one or more disadvantages. Therefore, there is a need to provide compositions and methods for improved packaging substrates for packaging of electronic circuits.

10 Summary of the Invention

The present invention is directed to compositions and methods for improved packaging substrates for packaging of electronic components. In one step, first and second precursors are provided having a backbone, and first and second ethynyl groups. In another step a crosslinker is provided having a first and a second reactive group. In a further step the crosslinker, the precursors, and a solvent are applied to a surface. In a still further step first and second ethynyl groups from first and second precursors are reacted with the first and second reactive group of the crosslinker in a carbon-carbon bond formation reaction, respectively, thereby crosslinking the first backbone with the second backbone. In yet a further step, the solvent is removed.

15 In one aspect of the inventive subject matter, the first and second precursor preferably comprise a phenyl group, and more preferably a phenylindane. The ethynyl groups of the first and second precursors preferably comprise an aryl group, more preferably is an arylethynyl group and most preferably is a phenylethynyl group. It is also preferred that first and second precursors are identical, at least in an oligomeric form, or that first and second precursors are covalently bound together via a bridging group.

20 25 In another aspect of the inventive subject matter the precursor further comprises an adhesion enhancer covalently bound to the backbone of the precursor. Also preferred is that the precursor comprises a halogen atom, and more preferred a bromine atom.

In a further aspect of the inventive subject matter a toughener, preferably a butadiene-type compound or acrylonitrile/butadiene-type compound, is added to the solvent containing the first and second precursor and crosslinker.

Various objects, features, aspects and advantages of the present invention will become
5 more apparent from the following detailed description of preferred embodiments of the invention, along with the accompanying drawings in which like numerals represent like components.

Brief Description of The Drawings

10 Fig. 1 is a prior art structure of a monomer for producing a packaging polymer.

Fig. 2 is a structure of one precursor according to the inventive subject matter.

Fig. 3 is a structure of another precursor according to the inventive subject matter.

Fig. 4 is a synthetic scheme of a precursor according the inventive subject matter.

Fig. 5 shows various embodiments of bridging groups according to the inventive subject
15 matter.

Detailed Description

As used herein, the term "backbone" refers to a portion in a molecule, onto which various substituents may be covalently bound. The backbone generally comprises more than 2 carbon
20 atoms when the backbone is an aromatic compound. When the backbone is an inorganic compound, typically more than two atoms are found in the backbone. Moreover, the backbone may comprise repeating units. For example contemplated backbones include various organic polymer-type compounds including polyindanes, polyimides, polyesters and polyethers, polyether ketones, polyphosphazenes, polyether ether ketones, polysulfones, polyphenyleneoxides, but also monomer-type compounds including an indane, a phenyl group, and a vinyl group. Bonds or single atoms *per se* are not considered a backbone under the scope
25 of the present definition.

As used herein, the term "packaging substrate" refers to a composite comprising an oligomeric or polymeric material which is impregnated into a reinforcement (e.g. glass), wherein the oligomeric or polymeric material may be cured, or partially cured. It is contemplated that the packaging substrate can be used for the high density interconnection of semiconductors and other components in the electronic industry. Although such composites are particularly applicable to electronics, they can also be used in any application where there is a need for non-flammable, low CTE composites such as in aerospace applications.

As used herein, the term "precursor" refers to a molecule which is chemically reactive and can be covalently coupled to another precursor or non-precursor molecule. Contemplated precursors may include organic, organometallic, and inorganic monomeric, oligomeric, and polymeric molecules.

As used herein, the term "crosslinker" refers to a molecule with at least two chemically reactive groups that are able to react with two precursors such that one precursor will be covalently bound to the first reactive group of the crosslinker, and another precursor will be covalently bound to the second reactive group of the crosslinker. Appropriate crosslinkers may also be molecules with a single reactive group that can undergo more than one chemical reaction. It is further contemplated that crosslinkers may have multiple reactive groups and that such crosslinkers may therefore covalently bind multiple precursors. A crosslinker, as contemplated herein, is capable of interconnecting a plurality of precursors such that the resulting crosslinked precursors will form a network having a molecular weight approaching the sum of the molecular weights of the precursors and crosslinkers that participate in the crosslinking reaction. It should further be appreciated that contemplated crosslinkers and precursors can react intermolecularly or intramolecularly.

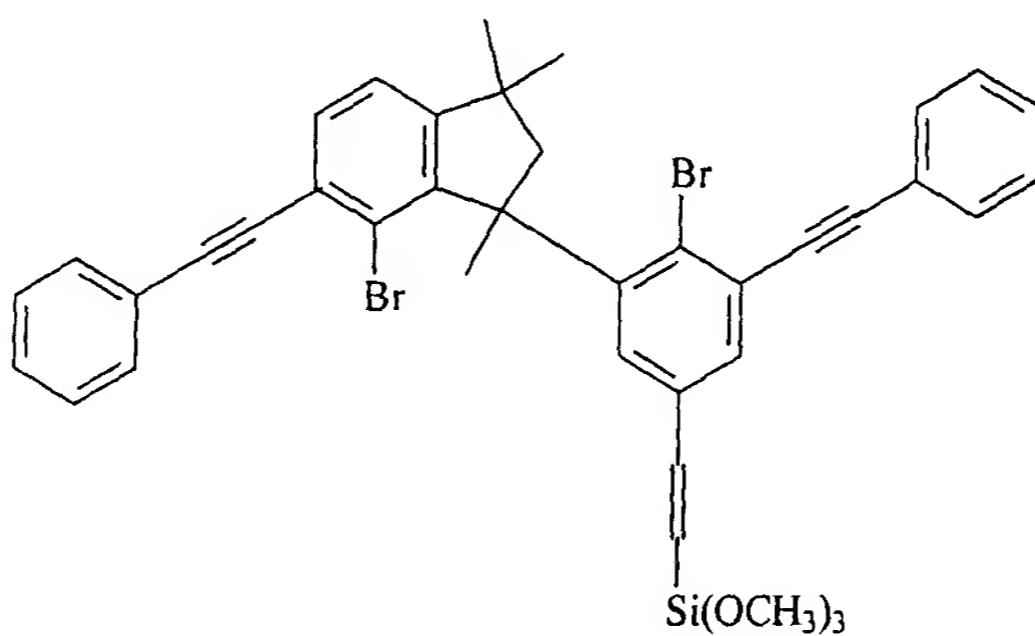
As used herein, the term "adhesion enhancer" refers to a molecule, that when covalently bound to another molecule increases the adhesion of the other molecule to a substrate. Especially contemplated substrates are dielectrics including glass, polymeric fibers, paper based dielectrics, etc., but may also include other substrates including metals and organic compounds.

As used herein, the term "toughener" refers to a compound that, when incorporated (i.e. intimately mixed or covalently bound) into a substrate, imparts increased resilience towards

mechanical challenges. For example, a toughener added to a compound may increase impact-, or scratch resistance, or may increase resistance to tear initiation and tear propagation.

Precursors

5 In one embodiment, the precursor has a backbone comprising a 1,1,3-trimethyl-3-phenylindane. Furthermore, the backbone comprises two aryl- and ethynyl groups, respectively, in the form of two phenylethynyl groups. The halogen atoms are two bromine atoms, which are covalently bound to the backbone. Also covalently bound to an aromatic portion of the backbone is a vinyl trimethoxysilane group as an adhesion enhancer (Structure 1).



10 With respect to the backbone, many compounds other than a 1,1,3-trimethyl-3-phenylindane are contemplated, including organic, organometallic and inorganic compounds. Appropriate organic compounds may comprise a substituted or unsubstituted alkyl, a substituted or unsubstituted aryl, a substituted or unsubstituted alkenyl, or an substituted or unsubstituted alkynyl. For example, such alternative compounds include an ethyl, isopropylidene, 15 fluoroisopropyl, ethenyl, 2-methyl-1,4-butadiene, propinyl, and 2-chlorobutinyl group. Further contemplated organic compounds may include saturated and unsaturated ring systems with at least one ring wherein the rings in a ring system may have any reasonable number of atoms, typically between 3 and 6. However larger ring systems are also contemplated, including fullerene-type structures and crown ether-type structures. It should further be appreciated that 20 alternative organic compounds need not be restricted to carbon atoms as the sole constituents, but may also include common heteroatoms, such as N, O, S, P, etc. For example, appropriate compounds include a phenyl, benzil, benzoxazole, indane, 1,1,3-trimethyl-3-phenylindane,

sulfone, benzobisimidazole, benzophenone, quinone, diphenylether, fluorinated anthracenyl groups, bismaleimides, phenyleneoxides, and so on.

Appropriate inorganic compounds may comprise substituted or unsubstituted metal oxides, including silicates, phosphates, alumina-type compounds, etc. For example, appropriate 5 compounds include silica, alumina, and orthophosphate. Contemplated organometallic compounds preferably include Si, however, other metals are also contemplated, including Al, PO₄, etc. For example, alternative compounds may include SiC, poly(dimethylsiloxane) and poly(vinylsiloxane).

It should also be appreciated that any reasonable combination of organic, inorganic, and 10 organometallic compounds may also be employed as alternative backbones, as well as oligomeric or polymeric forms of the aforementioned structures. Although many oligomeric and polymeric forms of backbones are contemplated, backbones comprising oligomeric 1,1,3-trimethylindanes are especially contemplated.

It is preferred that the backbone comprises at least two phenylethynyl groups, however, 15 the backbone may also comprise one, or more than two phenylethynyl groups. For example, alternative backbones may include 3-5 or more phenylethynyl groups. It is also contemplated that the phenyl and the ethynyl group are coupled to each other via a conjugated system. For example, such conjugated system may include a phenylethenylethynyl, and a naphtalylethynyl. Still further contemplated are backbones wherein the ethynyl group and the aryl group are 20 covalently bound to the backbone on different atoms of the backbone. For example, the ethynyl group may be bound to the phenyl portion of an indane, whereas the aryl group may be bound to the cyclopentenyl portion of the indane. In another example, the backbone may have only ethynyl groups and no phenyl group. Of course, when the ethynyl group and the aryl group are not covalently bound together, the number of individual aryl groups and ethynyl groups may vary 25 considerably.

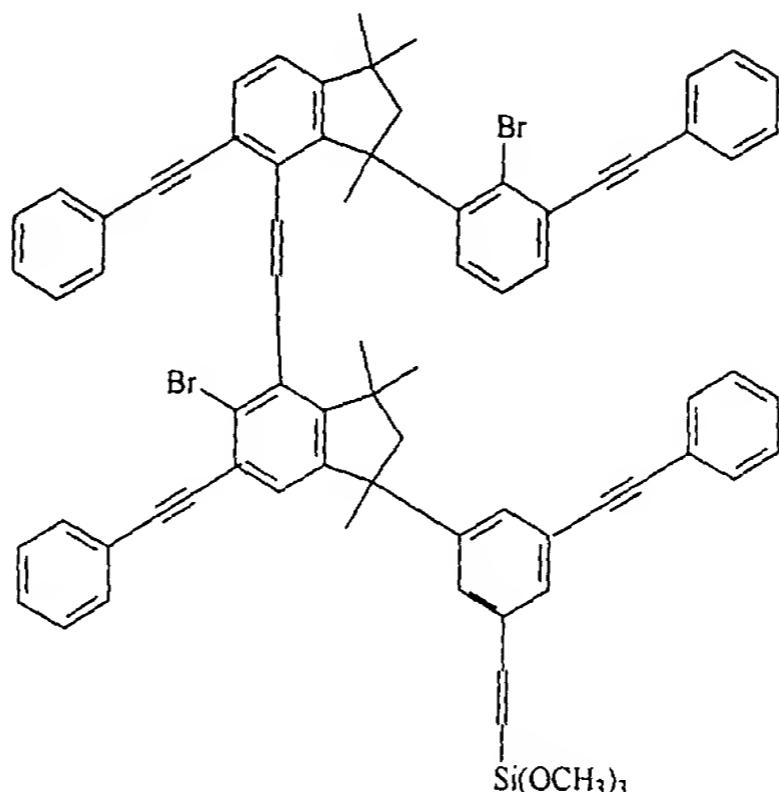
The halogen atoms bound to the backbone are preferably bromine atoms. Bromine is especially desirable because it confers non-flammability when covalently bound to an aromatic portion of the backbone. However, halogens other than bromine are also contemplated, including fluorine (which may reduce the dielectric constant), chlorine (which may confer increased

oxidative stability and flame retardance), and iodine. It should also be appreciated that various numbers other than two halogen atoms may be bound to the backbone. For example, alternative backbones may include one, but also three and more halogen atoms. Of course, also contemplated is any reasonable combination among different halogen atoms.

5 In a preferred embodiment, the adhesion enhancer is a vinyl trimethoxysilane. However, many alternative adhesion enhancers are also contemplated, including silanes and siloxanes. For example, appropriate adhesion enhancers include vinyltriethoxy silane, vinyltrimethoxy silane, vinylmethyldimethoxy silane, γ -methacryloxypropyltrimethoxy silane, vinyltriacetoxy silane, vinyl terminated siloxanes, and polysiloxanes. With respect to the attachment of the adhesion
10 enhancer to the backbone it is preferred that the adhesion enhancer is covalently bound to an aromatic portion of the backbone, however the adhesion enhancer may also be located on a different, non-aromatic portion of the backbone. It is further contemplated that not all of the precursors need to have an adhesion enhancer, and the amount of adhesion enhancer may vary. A preferred amount of adhesion enhancer is between 0.1% and 5% (by weight) and a more
15 preferred amount is between 0.3% to 3% (by weight). An exemplary structure of a precursor is shown in **Figure 2**, wherein X is F, Cl, Br, or I, y=0-3, y'=0-3 and y+y'>0, m=1-10, n=0-3, p=0-3, and E is an adhesion enhancer.

In another embodiment, the precursor has a backbone comprising two 1,1,3-trimethyl-3-phenylindane moieties covalently bound together via an ethylene group as a bridging group. Both
20 of the 1,1,3-trimethyl-3-phenylindane moieties are substituted with four aryl groups and four ethynyl groups configured in two phenylethynyl groups per 1,1,3-trimethyl-3-phenylindane moiety. The halogen atoms on the backbone are two bromine atoms, wherein one bromine atom is attached to one 1,1,3-trimethyl-3-phenylindane moiety, respectively. A vinyl trimethoxysilane

group is covalently bound to an aromatic portion of one of the 1,1,3-trimethyl-3-phenylindane moieties as an adhesion enhancer (see Structure 2).



With respect to corresponding elements between the precursors of structures 1 and 2, the
5 same considerations apply for precursor of structure 2 as discussed above. It should be
appreciated that although the precursor of Structure 2 comprises two almost identical backbones,
alternative structures with considerably different backbones are also contemplated.

It is preferred that the bridging group is an ethylene group, however, other bridging
groups besides an ethylene group are also contemplated, including an ethynyl group and various
10 divinyl compounds. Alternative bridging groups include diisopropenyl benzene, divinyl benzene,
various divinyl acrylates such as ethylene diacrylate, divinyl alkyldiacetate, various divinyl ethers
such as 1,4-butanediol divinylether, divinylsulfone, 1,3-divinyltetramethyldisiloxane, and
1,3,divinyl-1,1,3,3-tetramethyldisilazane. Other contemplated bridging groups are shown in
15 Figures 5A-H, wherein the bridging groups are divinylsulfone, 1,4-butanedioldivinylether,
ethylenediacrylate, 1,3-divinyltetramethyldisiloxane, 1,3-divinyl-1,1,3,3-tetramethyldisilazane,
divinylbenzene, 1,3-diisopropenylbenzene, respectively. It should be appreciated that the use of
bridging groups not only provides a cost-effective way of producing oligomeric precursors, but
also can be used to tailor the viscosity and ultimate properties of the desired polymer. It is further
contemplated that bridging precursors by employing bridging groups is preferably performed
20 such that the molecular weight of the resulting bridged precursors is about or less than 10,000Da,

and more preferably between about 500Da to 3000Da. However, higher molecular weights are also contemplated.

It is generally preferred that the precursors according to the inventive subject matter have more than one phenylethynyl group covalently bound to the backbone. However, it should be
5 appreciated that ortho-positioned phenylethynyl groups, although not excluded, are generally not preferred in the scope of the subject matter presented herein. More preferably, the phenylethynyl groups are randomly distributed on the aromatic portion of the backbone.

An exemplary structure of another precursor is shown in **Figure 3**, wherein X is F, Cl, Br, or I, y=0-3, y'=0-3 and y+y'>0, m=1-10, n=0-3, p=0-3, E is an adhesion enhancer, and L is a
10 bridging group. Further shown in **Figure 4** is an exemplary synthetic scheme of a brominated, phenylethynylsubstituted oligoindane precursor according to the inventive subject matter.

Methods of producing packaging substrates

In one preferred embodiment, a packaging substrate is prepared wherein in a first step
15 first and second precursors are provided in equal quantities, totaling 3.5g. Both the first and the second precursor are a brominated 1,1,3-trimethyl-3-phenylindane with four phenylethynyl groups covalently bound to the backbone wherein two of the phenylethynyl groups are bound in non-ortho position on the phenyl ring of the indane and another two phenylethynyl groups are bound in non-ortho position on the phenyl ring. In a next step, 5.8g of a mixture of
20 diphenylmethylenebismaleimide and diallylbisphenol A (commercially available as Kerimid 8292 (60% solids in n-methylpyrrolidinone) NMP60 from Ciba Specialty Chemicals) is provided as a crosslinker. In a further step the crosslinker, first and second precursor are dissolved in methyletherketone and propyleneglycolmethyletheracetate as a solvent and dip coated onto the surface of two plies of 4.5" x 5.5" 2116 woven glass. In a still further step, the carbon-carbon
25 bond formation between the reactive groups of the crosslinker and the ethynyl groups is achieved in a Diels-Alder reaction by reacting the first and second diene group with the first and second ethynyl group by prepping at 170°C for five minutes and subsequent laminating of the plies in a Carver press (6x6", 5000lb, heating at 240°C for 4 hours), whereby the first and second backbones are crosslinked and the solvent is concurrently removed.

In alternative embodiments, the precursors need not be provided in the same quantities. It is contemplated that many ratios (by molarity or by weight) are appropriate, including ratios of 1%-99% of the first precursor to 1%-99% of the second precursor. It is also contemplated that first and second precursor need not be limited to the same precursor, but may also be different.

5 Alternative precursors include a large variety of structures so long as such precursors comprise an aromatic portion and an ethynyl group. Appropriate precursors are discussed in the section precursors (Structure 1 - *vide supra*). In further alternative embodiments the precursors comprise first and second precursor covalently bound together by a bridging group. Similarly, appropriate bridged precursors are discussed in the section precursors (Structure 2 - *vide supra*).

10 In further alternative embodiments, the crosslinker need not be limited to a mixture of diphenylmethylenebismaleimide and diallylbisphenol A so long as alternative crosslinkers comprise a first and a second reactive group and are capable of formation of a carbon-carbon bond. Consequently, it should be appreciated that the mechanism of the carbon-carbon bond formation need not be limited to a Diels-Alder reaction, but may also include a 2+2 or a 4+2

15 cycloaddition, a free radical reaction, an ene-reaction, a Glaser coupling or a Straus coupling. It is generally preferred that alternative crosslinking moieties do not contain polar functionalities, which could possibly lead to increased absorption of moisture. It is further contemplated that alternative crosslinking moieties are hydrocarbon based, and that crosslinking occurs via a carbon-carbon bond formation reaction such that high glass transitions can be obtained. Thus,

20 alternative crosslinkers may include benzocyclobutanes, various 3-4 atom strained rings including aziridines, diketenes, biscyanate esters, etc., bifunctional vinyl aromatic compounds, trifunctional vinyl aromatic compounds, and multifunctional vinyl aromatic compounds. For example, appropriate crosslinkers include benzocyclobutane, divinylbenzene, and trivinylbenzene.

25 Of course, it should be appreciated that the quantities of employed first and second precursor and crosslinker may vary considerably depending on the type of application. Small scale application may require milligram quantities, whereas larger scale applications may need gram to kilogram quantities.

30 Although the solvents in preferred embodiment are methyletherketone and propyleneglycolmethyletheracetate, many alternative solvents are contemplated. Generally,

appropriate solvents are single solvents or solvent systems that are capable of at least partially dissolving first and second precursor and the crosslinker. However, other factors, including conditions of application, application quality and thickness, and end-use application influence the selection of an appropriate solvent. Representative solvents include hydrocarbons such as 5 xylene, toluene, mesitylene, but also halogenated hydrocarbons such as dichloromethane or chlorobenzene. Further appropriate solvents may include esters, ketones, ethers, and so forth. It should also be appreciated that some applications may be performed without a solvent. Such applications may for example employ powdered or granulated first and second precursor and crosslinker.

10 In still further alternative embodiments, many impregnation techniques other than dip coating are contemplated, including various coating, printing, casting, or spraying techniques depending on the material, size and quality of the surface whereupon the first and second precursor and crosslinker are to be applied. Alternative application techniques include among many others knife coating, roll coating, screen printing, spin coating, solution casting, spraying 15 etc.

20 In yet further alternative embodiments, the dielectric or reinforcing dielectric need not be restricted to 4.5" x 5.5" 2116 woven glass. Alternative reinforcements include lightweight woven glass fabric, for example 101 glass with an individual fiber diameters range from 5-6.0 microns. Further alternative reinforcements include unidirectional crossplies, crossplies of 25 unidirectional tape, film, fiber, or paper, and nonwoven papers. Nonwoven papers are desirable because of their uniformity, giving them superior lasing characteristics. Nonwoven paper can be prepared from staple fiber (otherwise known as floc), pulp, or a combination of staple and pulp. Staple fiber is generally referred to the longer fibers, whereas pulp is used to describe the shorter fibers. In general, longer staple has the advantage of better CTE control but leads to greater non-uniformity on the micron scale. Fiber pulp is generally obtained by chopping the fiber into very short fibers which are more uniform, have higher surface area, and typically absorb higher levels 25 of moisture. Examples of nonwoven paper include those prepared from microfine glass, ceramic fibers, silica fibers, quartz, PTFE filaments, organic fibers such as liquid crystalline fibers, and natural fibers.

In other alternative dielectrics, organic fibers can be used. Poly(p-phenylene terephthalamide), known as Kevlar® and poly(1,3-phenylene isophthalamide), sold as Nomex® [Tokarsky, US 4,729,921, Kirayoglu et al, US 5,314,742] are used to produce an all-aramid nonwoven paper, sold by Du Pont. Polyaramids as a class of organic polymers are especially suited for these applications due to their inherent low CTE's. Copolyaramids prepared from meta and para-phenylenediamine, terephthalic acid, isophthalic acid, and 3,4-oxydiphenylenediamine, more specifically copoly(para-phenylene/3,4'-oxydiphenylene terephthalamide, Technora®) are particularly useful (Teijin Limited, US 5,783,039). Liquid crystalline organic fibers which are useful as a reinforcement include Vectra® based on hydroxynaphthoic acid and hydroxybenzoic acid. Another preferred organic fiber is PBO, or poly(p-phenylene-2,6-benzobisoxazole) available as Zylon® by Toyobo Co, Ltd., Shiga, Japan. It is preferred over polyimide due to its lower moisture absorbing properties. Where the dielectric is a film, Kapton® (available from DuPont) and Upilex® (available from UBE Industries) are particularly preferred.

Although it is preferred that reacting the first and second ethynyl group with the first and second reactive group in a carbon-carbon bond formation reaction occurs preferably during the prepegging and laminating by applying thermal energy, various other reacting conditions are contemplated. For example, alternative energy sources may include UV-, VIS-, electromagnetic-, or particle radiation, exothermic chemical reactions, etc. It should also be appreciated that carbon-carbon bond formation reactions may occur between a crosslinker and two ethynyl groups of the same precursor, but more preferably between a crosslinker and a first ethynyl group of a first precursor and the same crosslinker and a second ethynyl group of a second precursor. Moreover, additional crosslinking may occur within a precursor or among more than one precursor in such cases where, for example phenylethynyl groups, are in ortho position to each other on an aromatic portion.

It should also be noted that by employing crosslinkers as coresins (e.g. benzocyclobutane), the thermal energy required to crosslink backbones is significantly reduced. For example, crosslinking in preferred embodiments generally occur at temperatures well below 250°C, whereas crosslinking of homopolymerized phenylethynyl functionalized aromatic compounds typically occurs at elevated temperatures of approximately 250°C-375°C [A. B.

Morgan, J. M. Tour, *Macromolecules*, 1998, 31, 2857]. By the same token, it is contemplated that various energetically favorable reactions other than a carbon-carbon bond formation reaction may be employed for crosslinking, including nucleophilic addition to triple bonds by di- or multifunctional nucleophiles, redox reactions between a crosslinker and pendent groups of a 5 precursor, entropically favored reactions (e.g. generation of N₂ driving the reaction) between crosslinker and pendent groups, and so forth.

With respect to removing the solvent, various techniques other than concomitantly removing solvent during prepegging/laminating are contemplated. Such alternative techniques include, but are not limited to baking the crosslinked backbones, vacuum drying, extraction with 10 another solvent, etc.

Additives

It has been found that some tougheners can advantageously increase mechanical stability and flexibility of a packaging substrate according to the present inventive subject matter when 15 added to the first and second precursor and crosslinker. Moreover, the addition of such tougheners typically does not compromise the glass transition temperature of the resulting packaging substrate. The resulting packaging substrate is more flexible, has a lower initial modulus relative to the equivalent non-toughener reinforced packaging substrates, yet has little or no thermal transitions between room temperature to 250°C. The modulus versus temperature 20 remains substantially flat across this range, as well as the coefficient of thermal expansion. Preferred tougheners include butadiene- and butadiene/acrylonitrile based rubbers, however, other tougheners are also contemplated, many of which are well known to the art.

Depending on the desired end product, alternative packaging materials may further include dielectrics as described above, augmented with various inorganic fillers. Such fillers may 25 include silica based nanospheres, hollow glass spheres, solid glass spheres, fused spherical silica, mica short chopped fibers, clay, talc, TiO₂, strontium titanate, which are used to enhance the dielectric constant and dielectric loss. Further contemplated fillers are ceramics, including boron nitride, silicon carbide, and beryllium oxide, which are known to enhance thermal conductivity.

In case of a woven or nonwoven glass-type dielectric, it is desirable that the fabric contain a binder, preferably a low moisture absorbing binder that facilitates polymer bonding to the reinforcing material. Binders or coupling agents are sometimes employed to improve bonding of filaments to other filaments within the reinforcement. It is also desirable that there is

5 good interfacial adhesion between all components of the reinforcement and resin system, such that the material does not fail during reliability testing such as solder reflow (simulates the placement of a semiconductor onto an electronic package such as a flip chip ball grid array, or a rework process) or pressure cooker testing (simulates long term exposure of electronic package to moisture). Silane binders are typically added during the weaving process. The binder is

10 applied to the fabric before resin impregnation, and should be present in sufficient quantity to completely coat all of the reinforcing materials fibers. Examples of useful silane based binders and coupling agents include CS718, CS767, and CS440, (manufactured by Clark-Schwebel, Inc), γ -aminopropyltriethoxysilane, γ -glycidoxypolytrimethoxysilane, β -(3,4-Epoxy)cyclohexyl ethyltrimethoxysilane, triethoxyvinylsildane, and hexamethyldisilazane. Binders may also

15 include epoxy resins (e.g. multifunctional epoxies with aromatic diamines such as DDS), elastomer adhesives (ChemlocTM), fluoroepoxies, "low Tg" resins such as acrylics, urethanes, aziridines, triazines, vinyl esters, rubbers, and so forth. It has been found that polyvinylmethylether is a particularly effective binder.

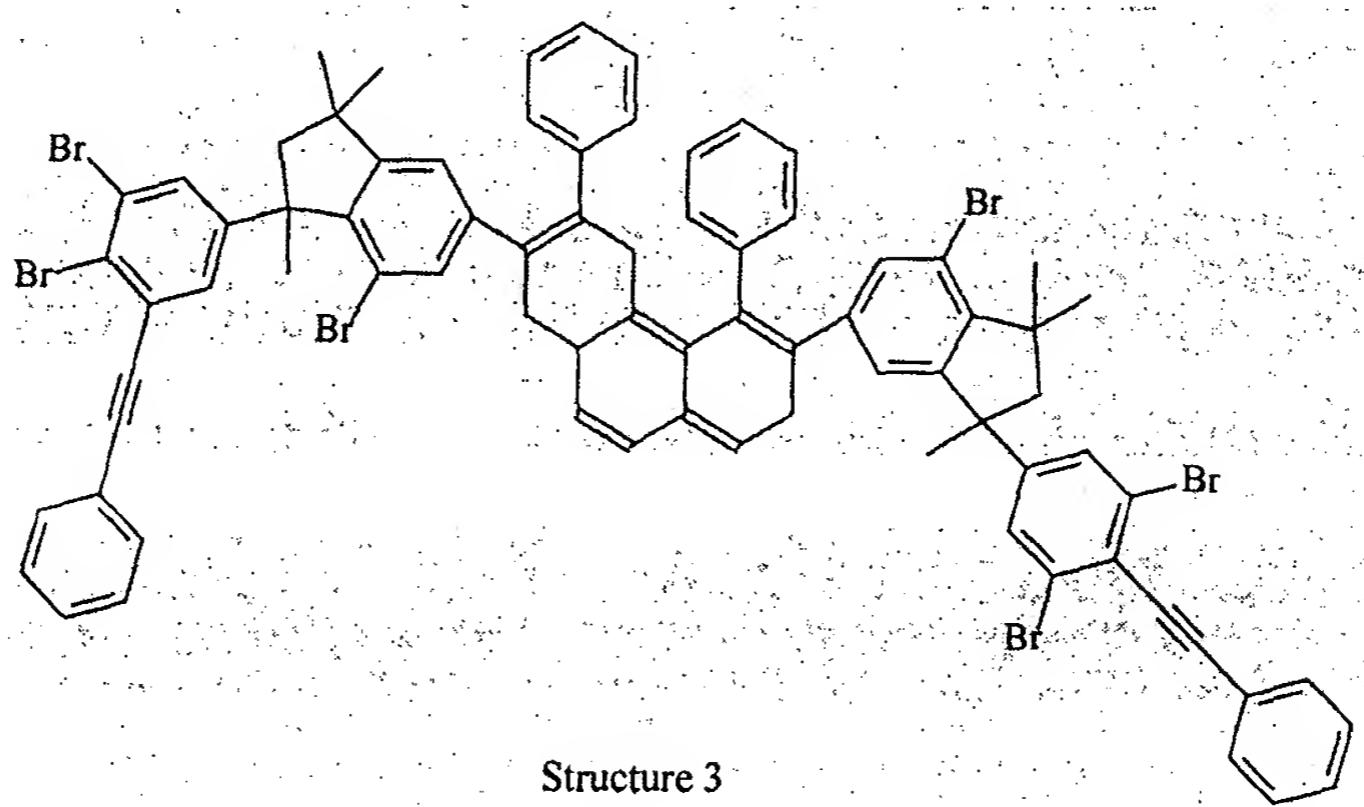
In the case of organic fiber-type dielectrics, it is often desirable to use much higher levels

20 of binders, with levels reaching up to 20% (by vol.) or more. Preferred binders for organic fibers include polyaramides, such as Nomex[®], precursors of polybenzoxazole with less than 100% ring closure, and polyamic acid precursors to polyimides. In some cases it might even be desirable to treat the surface of the dielectric/binder system before the first and second precursor and crosslinker are applied. Contemplated treatments might include plasma-, corona etching, ion

25 bombardment, but also solvent etching, and mechanical etching including sandblasting. Further contemplated treatments include chemical etching (e.g. chromic acid, permanganate, SO_3 , Na_2O_3), electron beam exposure, and deposition of carbon/diamond like coatings.

Properties of packaging substrates according to the inventive subject matter

An exemplary flame retardant packaging substrate fabricated according to the herein presented method is shown in Structure 3 (reinforcing dielectric omitted). The first and second backbones are both a brominated phenylethynyl substituted trimethylindane, crosslinked with the 5 crosslinker divinylbenzene. A first phenylethynyl group from the first backbone, and a first reactive aromatic vinyl group from the crosslinker divinylbenzene form a first carbon-carbon bond, and a second phenylethynyl group from the second backbone and a second reactive aromatic vinyl group from the same crosslinker form a second carbon-carbon bond.



10 The crosslinked, phenylethynyl functionalized brominated aromatic is shown partially cured and is intended to demonstrate the type of reaction that may occur during the prepegging step. Because there are various other carbon-carbon bond forming reactions possible which may lead to various other molecules than shown in exemplary structure 3, structure 3 is shown by way of example, and is not intended to limit to a particular structure. The packaging 15 substrates produced according to the herein presented method are generally contemplated to have a Tg of about 250°C to 400°C, and it is especially contemplated that when the packaging substrates are produced with brominated indanes (*vide supra*) that such packaging substrates not only have a Tg of about 275°C to 375°C, but that they are also flame retardant due to their bromination. It should further be appreciated that the packaging substrate shown in Structure 3 20 need not be limited to having backbones comprising a brominated phenylethynyl substituted trimethylindane, or that such backbones are crosslinked with the crosslinker divinylbenzene. Alternative structures may include other backbones and other crosslinkers as described in the

sections "precursor" and "method of producing packaging substrates". Also contemplated are structures having more than one crosslinker covalently binding one or more than one backbone together. It should further be appreciated that intermolecular crosslinking reactions may occur between crosslinkers only, or phenylethynyl groups only, and crosslinking reactions may also 5 involve the bridging group.

The thickness of the resulting resin/binder/reinforcement laminate can be controlled by adjusting amount of the first and second precursor and crosslinker applied to the reinforcing dielectric. For example, in applications where microvias of about 2 mil depth are desired, the packaging substrate comprises between about 30-70% (by weight) first and second precursor and 10 crosslinker. This can be controlled by varying the coating thickness and concentration of the first and second precursor and crosslinker in the solvent when the dielectric is coated onto a reinforcing substrate.

Lasing of the packaging substrate may be carried out by a frequency tripled Nd:yag, ultraviolet, CO₂, or excimer laser. For larger holes (>3 mil) the CO₂ laser is preferred, while the 15 Nd:YAG is well suited for 1-3 mil vias. Although lasing is a convenient way of manufacturing microvias, plasma generated holes and mechanically drilled or punched holes are also acceptable.

The electronic packaging substrates will have a CTE closely matched to that of copper (in the x and y directions). The packaging substrates typically have a x, y - CTE between that of 20 silicon and copper, ranging from 2 – 17 ppm/°C, but may also have a CTE in the range between 2 – 25 ppm/°C, or higher. The moisture absorption is generally lower than 1% (by weight), 0.0%5 being typical.

Examples

25 The following examples describe the synthesis of various precursors according to the inventive subject matter and the preparation of electronic package material thereof.

Example 1A

Preparation of oligotrimethyl phenyl indane (DIPB:AMS = 1:1)

To a 5 liter 3 necked round bottom flask equipped with an air driven mechanical stirrer
5 was added 800 g of dry 1,2-dichloroethane and 20 g of trifluoroacetic acid. 209.0 g of 1,3-
diisopropenylbenzene (1.32 mol) and 150.8 g of α -methylstyrene (AMS) (1.27 mol) were
combined in an addition flask, and were added dropwise to the stirred solution over a 1 hr time
period. After 1 hr of agitation in which the solution turned a light red color, 20 g of concentrated
sulfuric acid was added dropwise. The vessel was cooled externally with ice water to maintain a
10 temperature close to room temperature. The flask was allowed to stir overnight. 1 L of 10%
basic NaOH in water was added to the flask, the 1,2-dichloroethane distilled away causing the
precipitation of a solid, the product filtered and washed with deionized water, and then dried. 1 H
NMR analysis showed the presence of no internal olefins and the structure was consistent with
the literature [Dittmer, T., Gruber, F., Nuyken, O., *Makromol. Chem.* 190, 1771-1790 (1989)].
15 Integration of the protons showed a ratio of 1.95 : 1.0 aliphatic protons to aromatic protons.

Example 1B

Bromination of 1A

75 g of 1A was refluxed in 250 g CCl_4 with stirring in a 1 L 3 neck flask equipped with a
20 reflux condenser. 111.73 g of Br_2 was added slowly dropwise through an addition funnel located
above the reflux condenser in such a way that bromine did not carry over through the nitrogen
outlet located above the addition flask. A nitrogen inlet was fed into one of the necks of the 3
neck flask. Halfway through the bromine addition, 1 g of pyridine was added. After one day of
reflux, the flask was cooled and residual bromine was neutralized by the addition of a 10% KOH
25 aqueous solution. CCl_4 was removed by evaporation under reduced pressure. The solid was dried
yielding 91 g of product. Bromine analysis indicated an insufficient level of bromination. The
bromination was repeated at room temperature using 1.4 g of iron powder and 55 g of bromine.
After the dropwise addition of bromine, the temperature was raised to 60°C. Isolation of the
product and vacuum drying yielded 100.3 g of product having 42.80% bromine as determined by

bromine analysis. $^1\text{H-NMR}$ Integration of the protons showed a ratio of 2.17 : 1.0 aliphatic protons to aromatic protons.

Example 1C

5 Conversion of 1B to phenylethynl substituted brominated oligoindane 1C

50 g of 1B was dissolved in 180 g of anhydrous DMF and 210 ml of triethylamine in a 1L 3 neck flask equipped with an addition funnel, a reflux condenser, and a rubber septa through which a cannula was inserted with a nitrogen purge. The vessel was heated to 90°C and the contents were purged with nitrogen for one hour to remove oxygen. To the vessel was added 3.0 g of dichlorobis-(triphenyl-phosphine)palladium (II), followed by the dropwise addition of 20 g of phenylacetylene. The vessel was heated at reflux for 3 hours after which an additional 2 g of dichlorobis(triphenyl-phosphine)palladium (II) was added and 5.0 g of phenylacetylene. The vessel was allowed to reflux 3 additional hours. The vessel was allowed to cool, after which 600 ml of methylene chloride was added. The organic solution was washed 3x with 0.5 L of a 10% HCl aqueous solution and separated each time, washed 2x with water, the organic phase separated and filtered, the black product reduced to dryness under low vacuum, dissolved in 300 ml THF, precipitated into water, filtered, vacuum dried, yielding 59.0 g of product. Bromine analysis yielded a 12.92% bromine content which is a marked reduction from the 42.8% of the starting material indicating a substitution of phenylethynl for bromine. $^1\text{H NMR}$ Integration of the protons showed a ratio of 1.0 : 1.26 aliphatic protons to aromatic protons, which is consistent with the replacement of phenylethynl groups from bromine atoms. The proton spectrum was consistent with the oligoindane known in the literature, although the aliphatic protons were much broader and less resolved, and the aromatic region was rather complex. The following $^1\text{H NMR}$ (CDCl_3) assignments can be made (ppm) for brominated phenylethynyl substituted poly 1,1,3-trimethyl-3-phenyl indane: phenylethynyl aromatic protons (7.53); aromatic protons derived from indane (7.26); 1,1,3-trimethyl, 6H (**m**, 1.06, 1.36); 1,1,3-trimethyl 3H (1.64);, 2H (2.0-2.4). Analysis by DSC (10°C/min) showed a weak exotherm from 70-125°C likely corresponding to a softening point and a very broad endotherm ranging from 160-270°C with a peak at 199.1°C (103.4 J/g).

Example 1D

Preparation of a packaging substrate from 1C and Bismaleimide/diallylbisphenol A:

3.5 g of 1C was dissolved in 3.49 g of methyletherketone, to which was added 5.833 g of Kerimid 8292 (60% solids in n-methylpyrrolidinone) NMP60 from Ciba Specialty Chemicals (a mixture of diphenylmethylenebismaleimide and diallylbisphenol A). The solution was coated onto two plies of 4.5" x 5.5" 2116 woven glass. The individual plies were prepped at 170°C for five minutes. The plies were stacked and laminated together in a Carver press (6x6", 5000lb) and heated at 240°C for 4 hours. Samples of laminate were cut into 1.3 x 5.0 cm strips and stacked together and measured in torsion using a Rheometrics, Inc., rheometer (RDS2:RSI Orchestrator), at 6.28 rad/sec, 0.5% strain, using an auto tension adjustment. A tan delta peak at 290°C was observed. Onset of modulus loss (G') was 250°C. This example demonstrates that brominatedphenylethynyl substituted polyindanes can be co-cured with bismaleimide/diallyl compounds, acting as a crosslinking group to yield a laminate having a very high glass transition temperature.

15

Example 2A

Preparation of polytrimethyl indane (DIPB:AMS = 0.5:1)

Oligoindane oligomers were prepared as in Example 1A. 133.91 (0.846 mol) g of DIPB was reacted with 200 (118.18 mol) grams of AMS. ¹H NMR analysis showed the presence of no internal olefins and the structure was consistent with the literature [Dittmer, T., Gruber, F., Nuyken, O., *Makromol. Chem.* 190, 1771-1790 (1989)]. Integration of the ratio of the aliphatic protons to the aromatic protons yielded a result of 1.45 : 1.0.

Example 2B

25

Bromination of 2A

Bromination of 2A was carried out in a similar fashion as described in 1B with some modification. 75 g of 2A was dissolved in 250 cc of carbon tetrachloride. At room temperature was added dropwise 58 g of Br₂. This solution was allowed to stir until evolution of HBr

ceased. 1.4 g of iron powder was then added. This was allowed to stir until the evolution of HBr ceased. 58 g of additional bromine was added slowly. After the evolution of HBr slowed, the flask was slowly heated to reflux and allowed to reflux until the evolution of HBr ceased. The vessel was cooled, after which a 10% NaOH aqueous solution was added (1L), followed by 5 the addition of excess diethylether. The organic layer was washed 3x with basic water, washed with water, separated, the organic phase filtered, reduced to dryness under vacuum, and then vacuum dried. Bromine analysis yielded 37.67 % Br. ^1H NMR integration of the ratio of the aliphatic protons to the aromatic protons yielded a result of 2.16: 1.0, correlating with the replacement of aromatic protons with bromine. The ^1H NMR proton spectrum was consistent 10 with published NMR spectra of polyindane, with significant line broadening occurring.

Example 2C

Conversion of 2B to phenylethynyl substituted brominated oligoindane 2C:

Conversion of 2B to 2C was carried out using the procedure of 1C. The wt% bromine 15 content dropped from the 37.67 wt% of 2B to 7.25%. The proton spectrum was consistent with the polyindane known in the literature, although the aliphatic protons were much broader and less resolved, and the aromatic region was rather complex. The following ^1H NMR (CDCl_3) assignments can be made (ppm) for brominated phenylethynyl substituted poly 1,1,3-trimethyl-3-phenyl indane: phenylethynyl aromatic protons (7.53); aromatic protons derived 20 from indane (7.35); 1,1,3-trimethyl, 6H (**m**, 1.07, 1.38); 1,1,3-trimethyl 3H (1.62-1.72),; 2H (2.10-2.55). Integration of the ratio of the aliphatic protons to the aromatic protons yielded a result of 1.0:1.25. Analysis by DSC (10°C/min) showed an exotherm at 71°C corresponding to a melting point and a very broad endotherm ranging from 145-280°C with peaks at 193.2 (88.61 J/g) and 240°C (32.3 J/g).

25

EXAMPLE 2D

Preparation of a packaging substrate from 2C and Bismaleimide/diallylbisphenol A

6.66 g of 2C was dissolved in 5.96 g of methyletherketone, to which was added 5.5 g of Kerimid 8292 NMP60 (60% solids in NMP). The solution was coated onto two plies of 4.5" x

5.5" 2116 woven glass. A laminate was prepared using the procedure of 1D. A tan delta peak at 298°C was observed. Onset of modulus loss (G') was 262°C. This example demonstrates that when the brominatedphenylethynyl substituted indane is the major component of the formulation and the bismaleimide/diallylbisphenol A is present as a crosslinking component, a very high 5 glass transition temperature can be obtained.

Example 3A

Preparation of oligotrimethyl indane (DIPB:AMS =1.5:1)

Oligoindane oligomers were prepared using the apparatus and procedure of Example 1A 10 with the following modifications. After addition of TFA to carbon tetrachloride, the reaction flask was heated to reflux. 200.0 (1.26 mol) g of DIPB was combined with 99.27 (0.84 mol) grams of AMS and added dropwise over a period of 1 hour, after which the vessel was held at reflux a further four hours. A small sample was isolated and dried and showed a small degree of unsaturation remaining, the presence of internal olefins being observed from 4.8-6.2 ppm. 20 g 15 of sulfuric acid was then added dropwise and the vessel was allowed to reflux another day. ¹H NMR analysis showed the minor presence of internal olefins (< 5% of the protons could be assigned to vinylic protons (unsaturation), yet the structure was predominantly consistent with the literature [Dittmer, T., Gruber, F., Nuyken, O., *Makromol. Chem.* 190, 1771-1790 (1989)]. Integration of the ratio of the aliphatic protons to the aromatic protons yielded a result of 67.9 : 20 31.4.

Example 3B

Bromination of 3A

Bromination of 3A was conducted using the procedure of 1A. Bromine analysis showed 25 36.16% bromine. Integration of the ratio of the aliphatic protons to the aromatic protons yielded a result of 2.64:1, which is consistent with the replacement of aromatic protons with bromine. Otherwise the 1H NMR was consistent with the structure of polyindane as described in the literature.

Example 3C

Conversion of 3B to phenylethynyl substituted brominated oligoindane 3C:

Conversion of 3B to 3C was carried out using the procedure of 1C. The wt% bromine content dropped from the 36.16 wt% of 3B to 11.04%. The proton spectrum was consistent with the polyindane known in the literature, although the aliphatic protons were much broader and less resolved, and the aromatic region was rather complex. The following ¹H NMR (CDCl₃) assignments can be made (ppm) for brominated phenylethynyl substituted poly 1,1,3-trimethyl-3-phenyl indane: phenylethynyl aromatic protons (7.52); aromatic protons derived from indane (7.38); 1,1,3-trimethyl, 6H (m, 1.06, 1.37); 1,1,3-trimethyl 3H (1.66);, 2H (1.8-2.45). Integration of the ratio of the aliphatic protons to the aromatic protons yielded a ratio of 1.1:1.0. Analysis by DSC (10°C/min) showed a weak exotherm from 70-125°C likely corresponding to a softening point and a very broad endotherm ranging from 130-300°C with a peak at 193.0°C (103.4 J/g).

15

Example 3D

Preparation of a packaging substrate from 3C and Bismaleimide/diallylbisphenol A

6.66 g of 2C was dissolved in 5.96 g of methyletherketone, to which was added 5.5 g of Kerimid 8292 NMP60 (60% solids in NMP). The solution was coated onto two plies of 4.5" x 20 5.5" 2116 woven glass. A laminate was prepared using the procedure of 1D. A tan delta peak at 276°C was observed. Onset of modulus loss (G') was 238°C.

Example 4A

Conversion of brominated 1,1,3-trimethyl-3-phenylindane to brominated phenylethynyl substituted 1,1,3-trimethyl-3-phenylindane:

To a 3 neck 500 ml flask equipped with a reflux condenser, additional flask, and septum, was added 25 g of brominated trimethyl phenyl indane (commercially available from the Dead Sea Bromine Company, FR-1808, 73 wt% Br), 0.469 g of (+)-neomenthyldiphenylphosphine, 67 g of anhydrous acetonitrile and 67 g of triethylamine. The vessel was brought to 70°C and the

solution purged with nitrogen through a cannula directly into the solution for one hour. 0.0399 g of palladium (II) chloride was added and the environment was purged from above the organic layer with nitrogen. The vessel was brought to reflux after which 25.63 g of phenylacetylene was added dropwise. The color changed from initially green to increasingly purple/black.

5 Conversion of the brominated trimethylphenylindane, which was not very soluble in acetonitrile, to the brominated phenylethynyl substituted phenyl indane, which dissolved in acetonitrile, could be observed by the gradual dissolution of the starting material and the crystallization of triethylaminehydrogenbromide as fine needles. After refluxing for 18 hours, the vessel was cooled and diluted in a separate flask with 600 ml of diethylether. 30.7 g of salt was filtered
10 away. The organic phase was washed 3x with 10% HCl in water (700 ml), washed 2x with water, filtered, concentrated under reduced pressure, and vacuum dried yielding 32.0 g of product. Bromine analysis yielded 12.50% bromine which is a significant reduction from 73 wt% of the starting material. Palladium analysis indicated 0.053% (by weight) palladium in the product. The product was dissolved in MEK and passed through a commercial chelating ion
15 exchange resin, Reillex 402 polymer, a vinylpyridine based resin (available from Reilly Industries, Inc.), and after concentration and drying the product had a palladium content of 0.041%. Differential scanning calorimetry (10°C/min) of the product showed an exotherm at 92.9°C corresponding to sample melting, and a two endotherms at 246.2 and 292.3°C corresponding to the inter/intramolecular crosslinking of the phenylethynyl groups. The
20 following ¹H NMR (CDCl₃) assignments can be made (ppm) for brominated phenylethynyl substituted poly 1,1,3-trimethyl-3-phenyl indane: phenylethynyl aromatic protons (7.63); aromatic protons derived from indane (7.39); 1,1,3-trimethyl, 9H (series of multiplets, complex spectrum 1.5-2.3); 2H (2.6-2.9). Integration of the ratio of the aliphatic protons to the aromatic protons yielded a result of 1.0:1.25. Analysis by DSC (10°C/min) showed a weak exotherm at
25 90°C corresponding to a melting point and a very broad endotherm ranging from 160-340°C with peaks at 246.8 (183.2 J/g) and 288.8°C (143.1 J/g).

Example 4B

Preparation of a packaging substrates from 4A and benzocyclobutane

A solution was made containing to 16.8g 4A, 12.81 g MEK, 8.88 g benzocyclobutane (available from Dow Chemical as Cyclotene 3022-63 (BCB) which is a solution of 63% solids and 37% mesitylene), and 1.944 g Hycar 1300 x 33 butadiene/acrylonitrile rubber available from the BF Goodrich Co. The solution was divided into thirds. Each third was coated once onto two 4.5" x 5.5" sheets of 2116 woven glass with a Meyer rod, allowed to dry, and then recoated. After drying, the sheets were prepped at 230°C for five minutes. After prepping all laminates were prepared using a pressure of 5000lbs and four hours, 4B(230) heated at 230°C, 4B(240) 240°C, 4B(250) 250°C, 4B(250V) 250°C under vacuum. The laminate was pressed using a Carver press between stainless steel sheets separated by a teflon sheet for release purposes. Samples of laminate were cut into 1.3 x 5.0 cm strips and stacked together and measured in torsion using a Rheometrics, Inc., rheometer (RDS2:RSI Orchestrator), at 6.28 rad/sec, 0.5% strain, using an auto tension adjustment. Moisture absorption was measured according to JEDEC level 1 standards. Samples were predried at 125°C for one day to remove moisture. Samples were then weighed and placed in a humidity controlled oven (85% humidity, 85°C) and weighed on a daily basis until the weight remained constant. Wt% moisture was calculated based on the laminate. Wt% moisture gain based on the resin was obtained by ashing the laminate, determining the resin content, and assuming that the glass did not absorb moisture. A separate moisture measurement (Method 2) was made using a Hidden IGAsorp which consists of a moisture and temperature controlled oven. A sample is placed and weighed in a chamber and dried at 85°C with a dry nitrogen sweep until the weight comes to an equilibrium (the sample is dry), the humidity is then raised to 85% humidity and the sample is weighed until it comes to an equilibrium moisture gain. The sample is then dried using a similar procedure in order to calculate moisture absorption and desorption and the rate of absorption and desorption is recorded. Because all measurements are made *in situ*, there is little error. Method 2 showed very rapid absorption and desorption (<4 minutes) suggesting that the moisture being absorbed was not being absorbed by the resin or the glass but on the interface. A thicker 16 layer laminate 4B(250) showed equilibrium moisture absorption occurring in 9 minutes and desorption

occurring in 4 minutes. A sample of pure resin prepared according to the conditions of 4B (250) had a moisture absorption of 0.5% by method 2.

Sample	Onset of modulus loss/°C (G')	Tan delta Maximum /°C	Moisture absorption JEDEC (wt %)	Moisture absorption Method 2 (wt %)
4B(230)	250	307	0.15	0.66
4B(240)	270	>310	0.21	0.73
4B(250)	300	>350	0.14	0.95
4B(250V)	290	>350	-	

5 A similar solution was prepared on a larger scale to make a thick 1.6 mm laminate on 2116 glass using the conditions to prepare 4B(250). A bar was cut having the dimensions 1.6 mm x 1.0 cm x 5 cm and was measured using a Seiko DMA/TMA instrument in the three point bending mode (1 Hz, 3°C/min, under constant strain) where the sample was supported on it's ends and flexed in the middle perpendicular to the fiber directions which ran x,y. It therefore 10 probes especially the z axis. The tan delta maxima was not observed by 350°C. The onset of modulus loss was 249°C. A 0.7 cm² x 1.6 mm sample was measured by TMA in the expansion mode at 10°C/min using a quartz probe (aluminum standard). The z axis expansion showed two inflection points, one at 224°C and a larger one at 282°C. Z axis expansions were as follows 15 (ppm/°C): 20-150°C (40.4), 100-178°C (55.5), 245-260°C (260), 283-286°C (4,738). Total z axis expansion for the practical processing temperatures used in electronic packaging yielded 73.6 ppm/°C for 23°C-250°C. This example demonstrates that not only very high glass transitions can be obtained, but they can be obtained using an acrylonitrile/butadiene toughener which imparts flexibility to the laminate, yet does not compromise other key properties.

20 **Example 4C**

Conversion of brominated 1,1,3-trimethyl-3-phenylindane to brominated phenylethylnyl substituted 1,1,3-trimethyl-3-phenylindane

The experiment of 4A was repeated using 0.438 g of tris-o-tolylphosphine as a ligand instead of neomenthyldiphenylphosphine. The final product had 13.97 wt% bromine. This

example demonstrates that the coupling reaction of phenylacetylene to the brominated aromatic can be accomplished with the less expensive, more readily available, tris-*o*-tolylphosphine.

Examples 5A-C

5 **Preparation of a packaging substrate using brominated phenylethynyl substituted 1,1,3-trimethyl-3-phenylindanes and BCB:**

Electronic substrates were prepared from 1C, 2C, and 3C. A solution was made containing 5.6 g 1C, 4.27 g MEK, 2.96 g benzocyclobutane (available from Dow Chemical as Cyclotene 3022-63 (BCB) which is a solution of 63% solids and 37% mesitylene), and 0.648 g 10 Hycar 1300 x 33 butadiene/acrylonitrile rubber available from the BF Goodrich Co. Two sheets of 4.5 x 5.5" 2116 inch glass were coated, dried, and redried. Similar solutions were made using 2C and 3C. Laminates were prepared as in 4A and evaluated by DMA in the torsional mode as disclosed in 4A. Final press lamination was 4 hours at 250°C. These laminates were far stiffer 15 than the examples in 4A, having an order of magnitude initial higher modulus (G'). Although the onset of modulus loss occurred at lower temperatures for these samples, they exhibited much higher moduli across the whole temperature range. The tan delta curve for 5B can be described as almost flat with a barely discernable maxima at 320°C.

EXAMPLE	Resin	Onset of modulus (G') loss/°C	Tan delta maximum /°C
5A	1C	210	277
5B	2C	258	Very weak 320
5C	3C	230	294

Example 6A

20 **Conversion of brominated 1,1,3-trimethyl-3-phenylindane to brominated phenylethynyl substituted 1,1,3-trimethyl-3-phenylindane:**

6A was prepared using the procedure from 4A but with the following modifications. Bis(triphenylphosphine) palladium (II) dichloride was used as the catalyst. Final bromine content was 14.25%.

Example 6B

Preparation of a packaging substrate from brominated phenylethynyl substituted phenylindane and a PBO/glass Reinforcement:

5 A solution was prepared using 3.0 g Hycar 1300 x 33 butadiene/acrylonitrile rubber, 18.5 g Kerimid 8292 NMP60 (60% solids in NMP), 12.4 g MEK, 19.3 g propyleneglycolmethylether acetate, and 25.9 g 6A. The solution was coated with a Meyer rod onto a proprietary nonwoven fabric (6" x 6") consisting of microfiber glass, PBO pulp, and PBO staple. The laminate was prepegged for five minutes at 170°C in an oven and pressed at 230°C for 4 hours between two 10 polytetrafluoroethylene sheets sandwiched between two stainless steel plates. Laminates were prepared having 49% resin content. They were analyzed using a four camera CTE method over a temperature range from RT to 230°C. The software is designed to provide a temperature cycle which measures the spacings between the holes at room temperature, 40°C, and every 20°C interval up to 200°C where the temperature spacing is reduced to 10°C until 230°C. Before each 15 measurement, other than the initial room temperature measurement, the instrument stabilizes the sample for 10 minutes at temperature before the separations between the holes are measured. The x,y CTE for this laminate remained flat at 10 ppm/°C from RT to 100°C, after which it gently sloped up to 15 ppm/°C which was the maximum x,y CTE reached, and then gently sloped downward back to 9.5 ppm/°C by 230°C. This example demonstrates that very stable 20 low x, y CTE's can be obtained using the combination of a brominated phenylethynyl substituted polyindane and a PBO/microfiber glass reinforcement.

Example 7A

Conversion of brominated 1,1,3-trimethyl-3-phenyl indane to brominated, phenylethynyl substituted divinyl benzene bridged, oligomeric phenyl indane.

25 The experiment of Example 4A is repeated with the following modification: 0.3g of 1,4-divinyl benzene is added to the 25.63g of phenyl acetylene and the combined solution is added dropwise. The reaction is terminated after 11 hours by cooling and isolated according to Example 4A, with an expected yield of 31.0 grams of product. This example demonstrates that

an oligomeric divinyl benzene bridged, phenylethynyl functionalized, brominated aromatic can be prepared in a one convenient step process.

Example 8A

5 Conversion of brominated trimethylphenyl indane to brominated, phenylethynyl substituted, diisopropenyl benzene bridged, oligomer phenylindane.

The experiment of Example 7A is repeated with the following modification: 0.75g of 1,3-diisopropenyl benzene is used instead of 1,4-divinyl benzene. This example demonstrates that an oligomeric, 1,3-diisopropenylbenzene bridged, phenylethynyl functionalized, brominated aromatic can be prepared using 2.5% by weight of a bridging unit.

Example 9A

Conversion of brominated trimethyl phenyl indane to brominated phenylethynyl substituted, silicon containing phenyl indane.

15 The experiment of 4A is repeated with the following modification: 0.3g of vinyl-tris(beta-methoxyethoxy) silane is added to the 25.63g of phenylacetylene and the combined solution is added dropwise. The reaction is terminated after 10 hours by cooling and isolated according to Example 4A. This example demonstrates that a silicon containing functional group that is useful for adhesion to substrates, particularly glass, can be conveniently introduced into a 20 brominated, phenylethynyl aromatic compound. A laminate is prepared using the same process of Example 4B showing no tendency to blister during a prolonged pressure cooker test or solder float test.

Example 10A

Conversion of brominated trimethyl phenyl indane to brominated, phenylethynyl substituted, silicon containing phenyl indane.

5 The experiment of Example 9A was repeated with the following modification: 1.3g of vinyltriethoxysilane is used instead of tris(beta-methoxyethoxy)silane. A laminate is prepared using the same process of Example 4B showing no tendency to blister during a prolonged pressure cooker test or a solder float test.

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Example 11A

Conversion of brominated trimethyl phenyl indane to brominated, phenylethynyl substituted, silicon containing, oligomeric phenyl indane.

15 The experiment of 4A is repeated with the following modification: 0.5g of gammamethacryloxypropyltrimethoxy silane is added to the 25.63g of phenylacetylene, in addition to 0.75 g of 1,4-divinylbenzene and the combined solution is added dropwise. The reaction is terminated after 10 hours by cooling and isolated according to Example 4A. This example demonstrates that a silicon containing functional group that is useful for adhesion to substrates, particularly glass, can be conveniently introduced into a brominated, phenylethynyl oligomeric aromatic compound. A laminate is prepared using the same process of Example 4B showing no tendency to blister during a prolonged pressure cooker test or a solder float test.

20 This laminate is more flexible and showing a higher fracture toughness than comparable laminates produced from phenylethynyl, brominated aromatics having no bridging groups, or aromatics that are not oligomeric in nature.

Example 12A

Conversion of brominated trimethyl phenyl indane to brominated, phenylethynyl substituted, silicon containing oligomeric phenyl indane.

5 The experiment of 4A is repeated with the following modification: 1.2g of vinyltrimethoxysilane is added to the 25.63g of phenylacetylene, in addition to 0.75g of 1,3-diisopropenylbenzene, and the combined solution is added dropwise. The reaction is terminated after 10 hours by cooling and isolated according to Example 4A. This example demonstrates that a silicon containing functional group that is useful for adhesion to substrates, particularly
10 glass, can be conveniently introduced into a brominated, phenylethynyl oligomeric aromatic compound. A laminate is prepared using the same process of Example 4B showing no tendency to blister during a prolonged pressure cooker test or a solder float test. This laminate is more flexible and shows a higher fracture toughness than comparable laminates produced from phenylethynyl, brominated aromatics having no bridging groups, or aromatics that are not
15 oligomeric in nature.

Thus, specific embodiments and applications of improved packaging substrates have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted except in the spirit
20 of the appended claims. Moreover, in interpreting both the specification and the claims, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises", "comprising", and should be interpreted as referring to elements, components, or steps in a non-exclusive manner, indicating that the referenced elements, components, or steps may be present, or utilized, or combined with other elements, components,
25 or steps that are not expressly referenced.